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**PROBING STRUCTURE AND COMPOSITION OF  
NICKEL/TITANIUM CARBIDE HYBRID INTERFACES AT  
THE ATOMIC SCALE (Preprint)**

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## **Probing Structure and Composition of Nickel/Titanium Carbide Hybrid Interfaces at the Atomic Scale**

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### **Abstract**

The transition in structure and composition across the titanium carbide / nickel hybrid interface has been determined at near atomic resolution by coupling high-resolution transmission electron microscopy with three-dimensional atom probe tomography. The titanium carbide phase adopts a rocksalt-type structure, is highly non-stoichiometric with a composition of  $(\text{Ti}+\text{Ni})_2\text{C}$ , exhibits an orientation relationship with the nickel matrix with a structurally well-defined semi-coherent interface, and a compositionally distinct interfacial layer ( $\sim 2$  nm), that is marginally enriched in titanium and nickel and depleted in carbon.

### **Letter**

Hybrid materials based on a combination of metals and ceramics (also referred to as metal-ceramic composites) have drawn significant attention in recent years and are used in high temperature applications for chemical and nuclear reactors, wear and abrasion-resistant applications for high performance tools, as well as coatings for different engineering applications [1]. From the viewpoint of purely metallic materials, nickel-base alloys have been of considerable importance in a number of high temperature applications including aircraft jet engines, chemical/petrochemical plants, and will be of great importance in future generation nuclear reactor applications [2]. Carbide precipitates, such as those based on chromium or titanium carbides, often form the basis of enhanced creep resistance of nickel-base superalloys via grain boundary pinning [3]

and are also used (at higher volume fractions) in metal-matrix composites based on nickel [4]. The enhanced properties of these composites, which drive their application, are highly influenced by the metal-ceramic interfaces inherent in these hybrid materials. Thus, the study of the interface between nickel and titanium carbide, which can have a substantial impact on the high temperature microstructural stability, and attendant properties such as fracture toughness and creep resistance, is relevant both for metal matrix composites as well as nickel-base superalloys.

The stability of these hybrid interfaces is critically dependent on the structural conformity of the two phases at the atomic scale and the compositional partitioning of elements across the interface. Therefore, this study focuses on an atomic scale analysis of the transition in structure and composition across the metal/carbide interface in nickel-titanium carbide hybrid materials. The carbides in this material are in situ products forming from a reaction between titanium and carbon in molten nickel. Coupling two advanced characterization techniques, high-resolution transmission electron microscopy (HRTEM) and three-dimensional atom probe (3DAP) tomography, enables an analysis of the true structure and composition of these interfaces at sub-nanometer (near atomic) resolution.

The titanium carbide reinforced nickel based hybrid material used in this experiment was laser-deposited using the laser engineered net shaping (LENS) process with elemental nickel, titanium, and graphite powders as the feedstock. The LENS process involves rastering the laser beam on a solid substrate, creating a localized melt pool, into which powders of the desired composition are fed, and subsequently get rapidly solidified. A 500 W high frequency pulsed Nd-YAG laser emitting near-infrared laser radiation with a wavelength of 1.064  $\mu\text{m}$  was employed. The specific deposition parameters include 300 W laser power, a powder flow rate of  $\sim 2.57\text{g/min}$ , and a laser travel speed of 10 inches/min. Typical solidification rates encountered in LENS deposition lie in the range of  $10^2 - 10^3$  K/s. TEM/HRTEM analysis was done using an FEI TECHNAI F20 field emission gun (FEG) TEM operating at 200kV. Microtip specimens for atom probe were prepared using an FEI Nova 200 NanoLab dual-beam focused ion beam (FIB) system [5].

3D atom probe experiments were carried out using the Local Electrode Atom Probe (LEAP) system manufactured by Imago Scientific Instruments. The 3DAP experiments were carried out in laser-pulsing mode with an average evaporation rate of 0.5 ions pulse<sup>-1</sup>, specimen temperature of 100K and 0.8nJ pulse energy and the data was visualized and analyzed using the IVAS 3.0 software.

During laser deposition via the LENS process, the titanium and carbon (graphite) powders presumably dissolve within the molten nickel pool and subsequent rapid solidification results in the homogeneous precipitation of titanium carbides, typically < 500 nm in size, within the nickel matrix, as shown in the bright-field TEM image in Fig. 1(a). The carbide precipitates exhibit a faceted morphology with rounded corners in some cases. The strong diffraction contrast visible within the nickel matrix possibly arises from a high density of dislocations and strain resulting from the high cooling rates experienced during laser processing. Nevertheless, a high resolution TEM image shown in Fig. 1(b), clearly exhibits a relatively flat and planar carbide/nickel interface with the lattice planes visible in both phases. A Fourier-filtered image of the same interface, shown in Fig. 2(a), clearly exhibits a 4-fold symmetry about the [001] axis (viewing direction) in the carbide region, and confirms that the titanium carbide exhibits a  $\delta$ -TiC, rocksalt-type structure. The corresponding viewing direction for the face-centered cubic (FCC) nickel phase in the same Fig. 2(a) is the 2-fold [011] axis. The Fourier transform corresponding to Fig. 2(a) is shown in Fig. 2(c). Based on this Fourier transform as well as other selected area electron diffraction patterns, the orientation relationship between the  $\delta$ -TiC and FCC Ni phases was determined to be  $[100] \delta\text{-TiC} // [110] \text{FCC Ni}$  and  $(002) \delta\text{-TiC} // (-111) \text{FCC Ni}$ . The  $(-111)$  interplanar spacing for FCC Ni is 2.0 Å and that of (002) planes in stoichiometric  $\delta$ -TiC is 2.2 Å, with a misfit of 10%. The carbide/nickel interface plane appears to be oriented at an angle of 20° from the (1-11) planes of FCC Ni and at an angle of 30° from the (020) planes of TiC. Based on this analysis, the interface plane appears to be parallel to the (1-12) planes of FCC Ni. Theoretically the angle between (1-12) and (1-11) of Ni should be 19.4° that is in close agreement with the experimentally measured value. Additionally, the FCC Ni phase being substantially softer (lower elastic constants) as compared with the  $\delta$ -TiC phase, results in the partitioning of the elastic

strain arising from the misfit between the two phases more towards the FCC Ni phase. Consequently the FCC Ni matrix has a high degree of strain as clearly visible in Fig. 2(a). Furthermore, the strain at carbide/nickel interface, arising from the misfit between the two phases, is partially relieved by the formation of misfit dislocations at the interface, shown in the magnified view of the interface in Fig. 2(b), separating coherent regions of excellent lattice matching.

Nanometer scale analysis of the compositional transition across the carbide/nickel interface was carried out using 3D atom probe. Tomographic 3D atom probe reconstructions of C (blue), Ti (black), and, Ni (green) atoms within a region containing both the  $\delta$ -TiC and FCC Ni phases and the separating interface are shown in Fig. 3(a). The two phases each respectively constitute ~50% of the reconstruction volume (~ 40000 nm<sup>3</sup>) allowing for a statistically relevant qualitative and quantitative measurement of composition of the carbide phase. Some amount of titanium and carbon is present in the FCC Ni region (shown in green) and vice versa. Fig. 3(b) shows the carbide/nickel interface, clearly delineated by plotting a 30 at% C iso-concentration surface (isosurface in short). This interface is inclined at ~45° relative to the Z direction (along the reconstruction length) and consequently gives a good balance between the inherently high spatial resolution on 3DAP along the Z-direction, and, effects arising from local changes in evaporation field effects [6]. The interface has an average roughness  $S_a = 0.3$  nm, RMS roughness  $S_q = 0.36$  nm and area peak to valley  $S_t$  of 2.13 nm supporting the HRTEM results of the interface being relatively flat. The 30 at % C isosurface, shown in Fig. 3(b), has been used for calculating the proximity histogram composition profiles for Ni, Ti, and, C, across the interface. The steady-state compositions of the elements suggest that the  $\delta$ -TiC phase is highly non-stoichiometric with the contents of Ti, C and Ni being 59, 33, and, 7 at% respectively. Assuming Ti and Ni occupying the same sublattice in the  $\delta$ -TiC structure, the composition exactly matches (Ti+Ni)<sub>2</sub>C. This is rather interesting considering that the equilibrium Ti-C phase diagram [7] shows that the  $\delta$ -TiC phase can accommodate a high degree of non-stoichiometry, especially at higher temperatures. The FCC Ni phase has a negligibly small amount of Ti and C. The compositional gradient across the carbide/nickel interface is ~ 4 nm based on a 10-90 % of the steady state

composition method [8-9]. Additionally, within the interface region marked in Fig. 3(c), a marginal local enrichment of Ti and Ni, and a corresponding depletion in the C content is clearly visible on the  $\delta$ -TiC side, suggesting the possibility of formation of an interfacial layer or reaction product. While the high resolution TEM analysis (refer to Figs. 1(b) and 2(a)) did not exhibit any structurally distinct interfacial layer, the localized compositional change at the interface, revealed by the 3DAP analysis, possibly arises from an interfacial layer with similar crystal structure as TiC but a different composition. Ti enrichment in this interfacial layer is also visible in the high magnification Ti atom map, shown in Fig. 3(d).

Coupling HRTEM and 3DAP techniques, the structural and compositional transition across the titanium carbide/nickel ceramic-metal hybrid interface has been determined at near-atomic resolution. The far-from stoichiometric composition of the  $\delta$ -TiC phase, approximately  $(\text{Ti}+\text{Ni})_2\text{C}$ , indicates the high temperature of formation of these carbides during laser-deposition. While the carbide/nickel interface is a structurally well-defined semi-coherent interface with a distinct orientation relationship, there appears to be a compositionally distinct interfacial region enriched in Ti and Ni, while being depleted in C.

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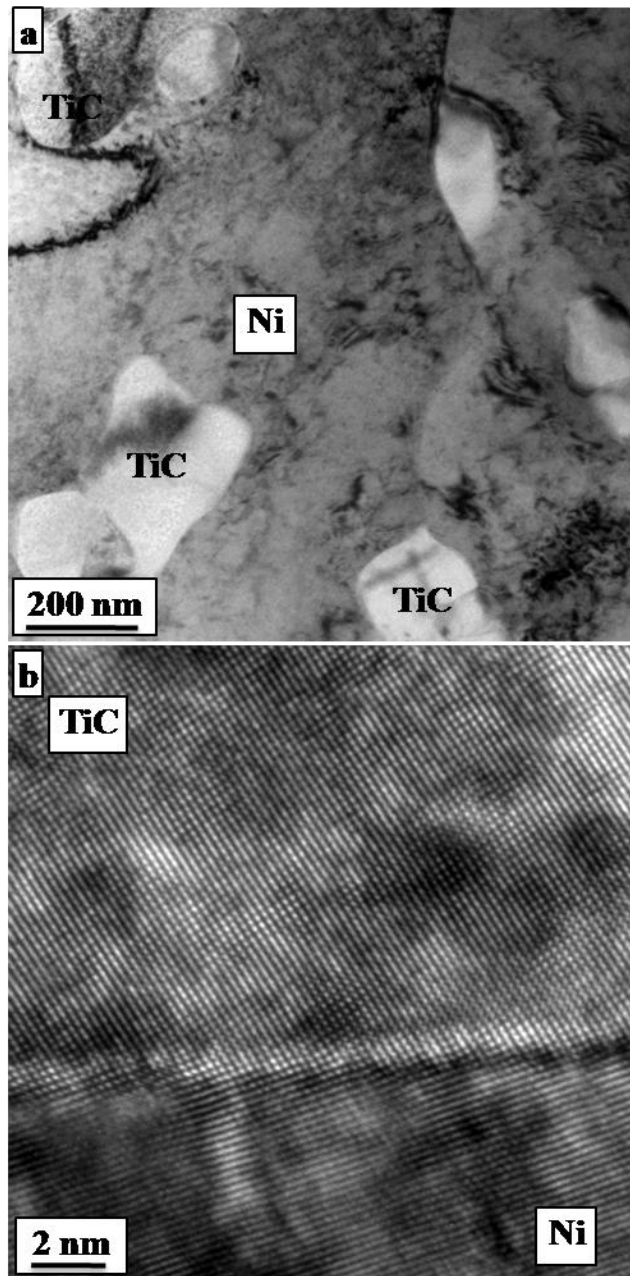


Fig. 1. TEM image (a) and HRTEM image of Ni and TiC interface.

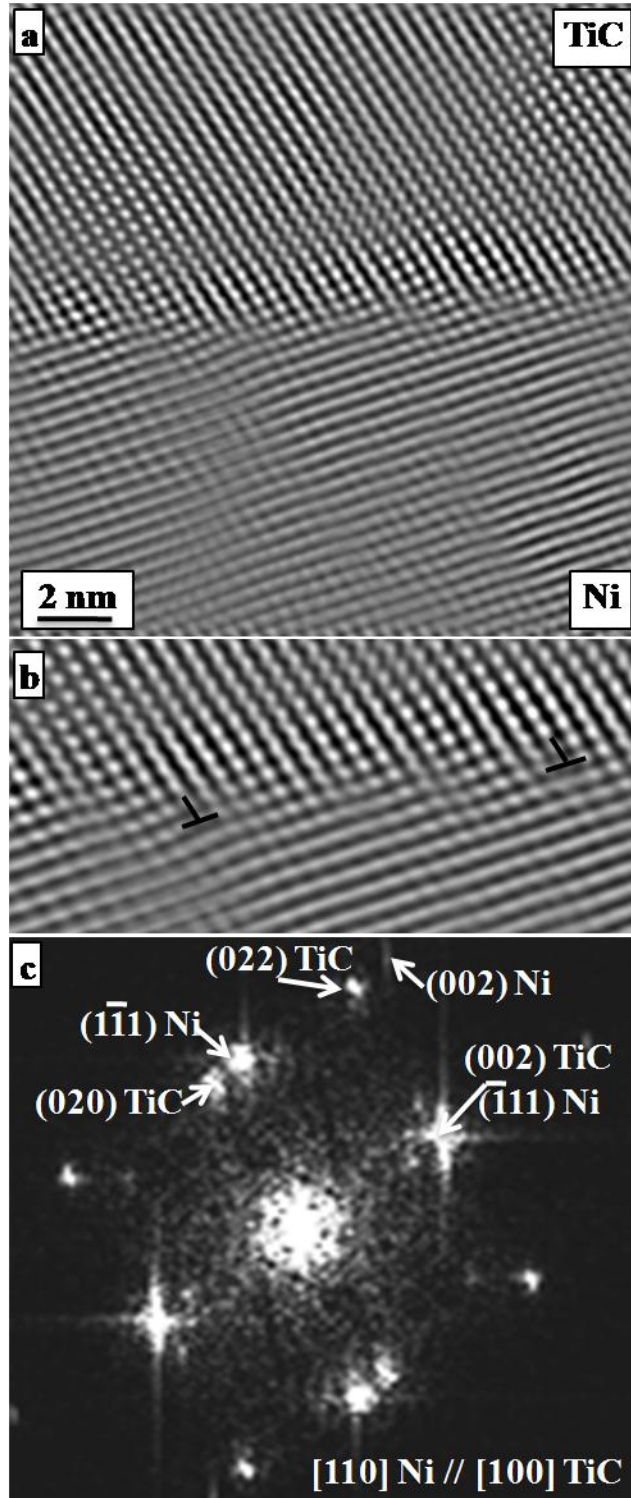


Fig. 2. Filtered HRTEM image (a), interface showing semi-coherent interface (b), and FFT pattern having specific orientation relationship (c).

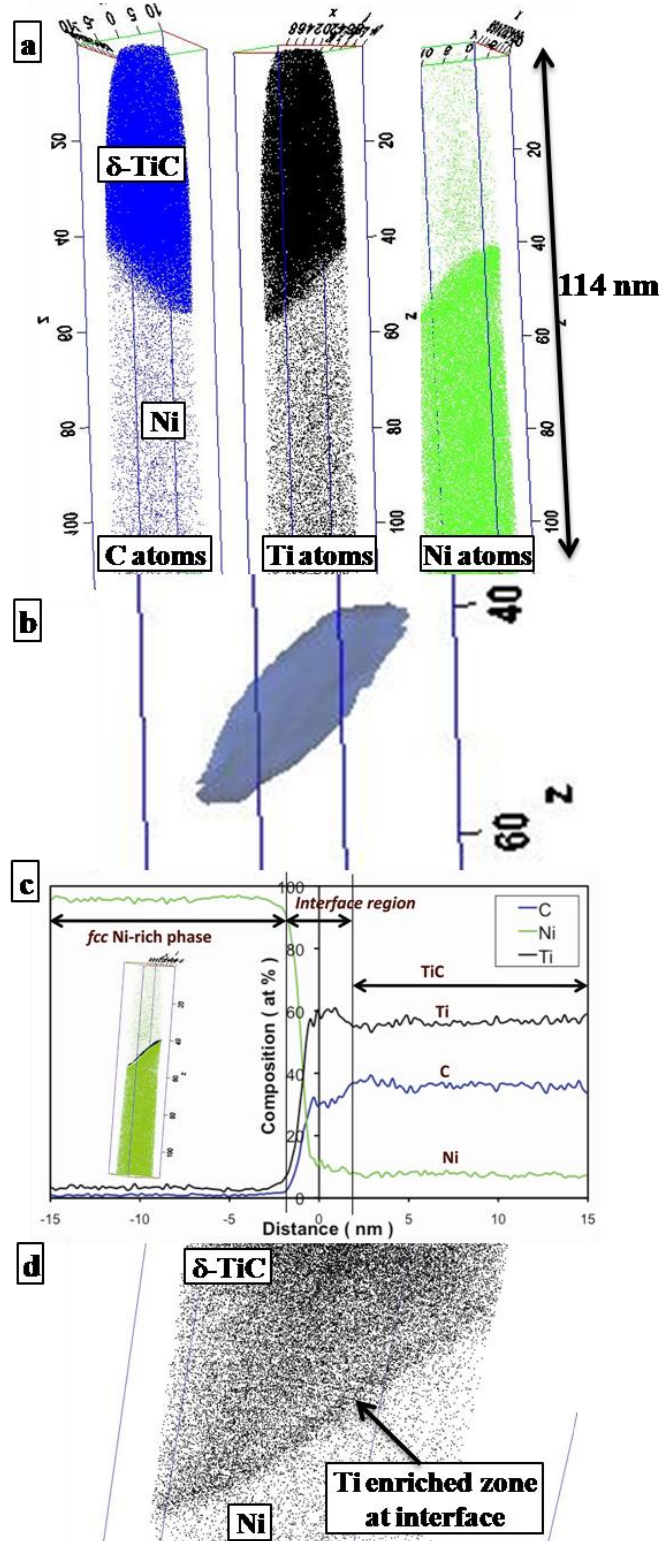


Fig.3. Atom probe results showing sharp interface between Ni/TiC interface (a,b), compositional profile along the interface (c), and higher magnification of the interface (d).